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Indian Standard
METHODS FOR CHEMICAL
ANALYSIS OF ROCK PHOSPHATE

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METHODS FOR CHEMICAL ANALYSIS OF ROCK PHOSPHATE

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Indian Standard

METHODS FOR CHEMICAL ANALYSIS OF ROCK PHOSPHATE

0. FOREWORD

0.1 This Indian Standard was adopted by the Indian Standards Institution on 27 June 1979, after the draft finalized by the Methods of Chemical Analysis Sectional Committee had been approved by the Structural and Metals Division Council.

0.2 In order to determine correctly the main constituents of rock phosphate, standard methods of analysis have been laid down in this standard. These methods may also be used for routine analysis.

0.3 In reporting the result of a test or analysis made in accordance with this standard, if the final value, observed or calculated, is to be rounded off, it shall be done in accordance with IS : 2-1960*.

1. SCOPE

1.1 This standard covers the methods for determination of phosphorus pentoxide, calcium oxide, fluorine and carbon dioxide in rock phosphate.

2. SAMPLING

2.1 The samples shall be drawn in accordance with IS : 1817-1961†.

3. QUALITY OF REAGENTS

3.1 Unless otherwise specified, pure chemicals and distilled water (*see* IS : 1070-1977‡) shall be employed in the test.

NOTE — 'Pure chemicals' shall mean chemicals that do not contain impurities which affect the results of analysis.

4. DETERMINATION OF PHOSPHORUS PENTOXIDE

4.1 Outline of the Method — Phosphorus is directly precipitated as magnesium-ammonium-phosphate in presence of ammonium citrate, ignited and weighed as magnesium pyrophosphate.

*Rules for rounding off numerical values (*revised*).

†Methods of sampling non-ferrous metals for chemical analysis.

‡Specification for water for general laboratory use (*second revision*).

4.2 Reagents

4.2.1 Concentrated Hydrochloric Acid — rd = 1.16 (conforming to IS : 265-1962*).

4.2.2 Concentrated Nitric Acid — rd = 1.42 (conforming to IS : 264-1968†).

4.2.3 Ammonium Citrate — solid.

4.2.4 Magnesia Mixture — Prepare magnesia mixture as follows:

Dissolve 400 g of magnesium chloride ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) and 300 g of ammonium chloride in 1500 ml of warm water. When solution is complete, add ammonium hydroxide until the solution is alkaline to litmus. Allow to stand for about one hour, filter, and add hydrochloric acid (1 : 1) to the filtrate until the solution is acid to litmus. If properly prepared, the volume of the solution is almost 2 litres.

4.2.5 Concentrated Ammonium Hydroxide — rd = 0.89.

4.2.6 Dilute Ammonium Hydroxide — 1 : 20 (v/v).

4.2.7 Dilute Hydrochloric Acid — 20 percent.

4.2.8 Citric Acid — solid.

4.3 Procedure

4.3.1 Transfer 0.5 g of a sample that has been dried at 105°C to a 500-ml Erlenmeyer flask, and add 15 ml of concentrated hydrochloric acid and 3 ml of concentrated nitric acid. Place a small cover glass over the mouth of the flask, and boil gently for 30 minutes. Rinse and remove the cover glass, and add 30 g of ammonium citrate, 10 ml of concentrated hydrochloric acid, and 100 ml of magnesia mixture. Neutralize the solution with concentrated ammonium hydroxide, using litmus paper as indicator, and add 3 ml of concentrated ammonium hydroxide in excess. Dilute the solution to 225 to 250 ml with water, add a few glass beads, stopper the flask tightly, shake vigorously for about one-and-a-half hours, and allow to stand overnight. Filter through a paper of close texture, and wash the flask and paper once with a small quantity of dilute ammonium hydroxide. Discard the filtrate.

4.3.2 Dissolve any magnesium ammonium phosphate remaining in the flask in about 50 ml of warm dilute hydrochloric acid and then pour the solution through the paper to dissolve the phosphate that was transferred to the filter and to separate any insoluble residue that may have remained

*Specification for hydrochloric acid (revised).

†Specification for nitric acid (first revision).

after the acid attack. Wash the paper and flask with more of the same acid, and add 0.3 g of citric acid and 1 ml of magnesia mixture to the solution, which should have a volume of about 100 ml. While stirring, slowly add concentrated ammonium hydroxide until the solution is alkaline to litmus, and then add 5 ml in excess. Stir occasionally during one-and-a-half hours, and allow to stand for 4 hours or overnight.

4.3.3 Collect the precipitate on a 9-cm paper of close texture, wash with cool dilute ammonium hydroxide and transfer the paper and precipitate to a weighed silica or porcelain crucible. Char the paper without flaming, burn off the carbon below 900°C and finally ignite to a constant mass, preferably in a muffle, at 1 050 to 1 100°C.

4.3.4 Make a blank determination using the same procedure and same quantities of reagents but without the sample.

4.4 Calculation

$$\text{Phosphorus pentoxide, percent} = \frac{(A - B) \times 63.78}{C}$$

where

A = mass in g of the magnesium pyrophosphate precipitate,

B = correction for the blank, and

C = mass in g of the sample taken.

5. DETERMINATION OF CALCIUM OXIDE BY THE OXALATE (VOLUMETRIC) METHOD

5.1 Outline of the Method — Calcium is precipitated as oxalate, filtered, washed, dissolved in hydrochloric acid and reprecipitated. This precipitate is filtered, washed, dissolved in sulphuric acid and titrated with standard potassium permanganate solution.

5.2 Reagents

5.2.1 *Concentrated Hydrochloric Acid* — See 4.2.1.

5.2.2 *Concentrated Nitric Acid* — See 4.2.2.

5.2.3 *Hydrofluoric Acid* — 40 percent.

5.2.4 *Sodium Carbonate (AR)* — solid.

5.2.5 *Dilute Hydrochloric Acid* — 1 : 1 (v/v).

5.2.6 *Ammonium Chloride* — solid.

5.2.7 *Dilute Acetic Acid* — 1 : 1 (v/v).

5.2.8 Ammonium Oxalate — solid.

5.2.9 Oxalic Acid Solution — 1 g/l (*m/v*).

5.2.10 Dilute Sulphuric Acid — 1 : 4 (*v/v*).

5.2.11 Standard Potassium Permanganate Solution (0.1 N) — Dissolve 3.2 g of potassium permanganate in 1 litre of water. Let stand in the dark overnight. Filter, without washing, through glass wool. Avoid contact with rubber or other organic material. Store in a dark-coloured glass-stoppered bottle. Standardize against standard sodium oxalate (AR).

5.3 Procedure

5.3.1 Transfer 0.5 g of the sample that has been dried at $105 \pm 5^\circ\text{C}$ to a 400-ml tall form beaker. Dissolve, by boiling gently with 20 ml of concentrated hydrochloric acid and 10 ml of concentrated nitric acid, until the volume is reduced to about 10 ml. Covering the beaker by a watch-glass throughout the process of dissolution, add 20 ml of concentrated nitric acid, and again evaporate to a small volume. Wash the lower surface of the watch-glass into the beaker with hot water, dilute the contents of the beaker with about 20 ml of hot water, filter and wash collecting the filtrate and washings in a 250-ml measuring or volumetric flask. Preserve the filter and washings.

5.3.2 Dry the residue and burn off the filter paper by ignition in a platinum crucible. Moisten the cooled residue with a few drops of concentrated nitric acid, and add about 10 ml of hydrofluoric acid. Evaporate continuously just to dryness, ignite and fuse the residue with about 2 to 3 g of sodium carbonate. Extract the melt in about 25-30 ml of dilute hydrochloric acid in a beaker, evaporate to dryness and bake. Extract the baked mass with about 10 ml of concentrated hydrochloric acid, dilute, boil, filter and wash collecting the filtrate and washings in the same volumetric flask wherein the first filtrate along with washings has been preserved (*see 5.3.1*). Cool the combined filtrates and make up to the mark.

5.3.3 Pipette out exactly 100 ml from the solution in the volumetric flask under **5.3.2** into a 400-ml beaker. Add sufficient ammonium chloride (about 15 g) to hold magnesium in solution in presence of ammonium oxalate. Add 20 ml of dilute acetic acid, heat to boiling and add with stirring about 2 g of ammonium oxalate. Boil and allow the precipitate to settle for 1 to 2 hours, cool and filter the solution through a close texture paper. Wash the precipitate with hot water until free from oxalate.

5.3.4 Dissolve the precipitate on the filter in about 50 ml of hot dilute hydrochloric acid. Wash the filter thoroughly with hot water until the filter is free from acid and collect the washings also in the same beaker

in which calcium was first precipitated. Reduce the bulk to about 100 ml by evaporation and reprecipitate calcium as oxalate as under 5.3.3.

5.3.5 Filter the precipitate and wash first with water containing oxalic acid or ammonium oxalate and then with water until the final washings are free from oxalate or oxalic acid.

5.3.6 Wash the precipitate of calcium oxalate into the same beaker in which precipitation was first carried out and treat the filter with about 25 ml of warm (70 to 80°C) dilute sulphuric acid for dissolving adhering precipitate of calcium oxalate. Wash the filter free from acid by means of hot water. Collect the washings also in the same beaker into which the precipitate was transferred. Add about 25 ml more of dilute sulphuric acid and raise the temperature of contents to about 70°C. When the precipitate has dissolved, titrate with standard potassium permanganate solution until a permanent pale pink colour persists in solution.

5.4 Calculation

$$\text{Calcium oxide, percent} = \frac{A \times B \times 0.028}{C} \times 100$$

where

A = volume in ml of the standard potassium permanganate solution,

B = normality of the standard potassium permanganate solution, and

C = mass in g of the sample represented by the aliquot taken.

6. DETERMINATION OF FLUORINE BY DISTILLATION METHOD

6.1 Outline of the Method — Fluorine is separated as hydrofluosilicic acid by distillation with perchloric acid and determined by titration against standard thorium nitrate solution using sodium alizarine sulphionate as indicator.

6.2 Apparatus

6.2.1 The distillation apparatus (see Fig. 1) consists of a 250-ml distillation flask (A), side arm of which is connected to a condenser (B). The neck of the flask is fitted with a two-holed rubber stopper carrying a thermometer (C) and 4 mm glass tube (D) connects the flask to a steam generator (E) which is equipped with two discharges, one tube (F) to release steam and the other (D) to deliver steam into the distillation flask (A). The distillate is collected in a Erlenmeyer flask (G).

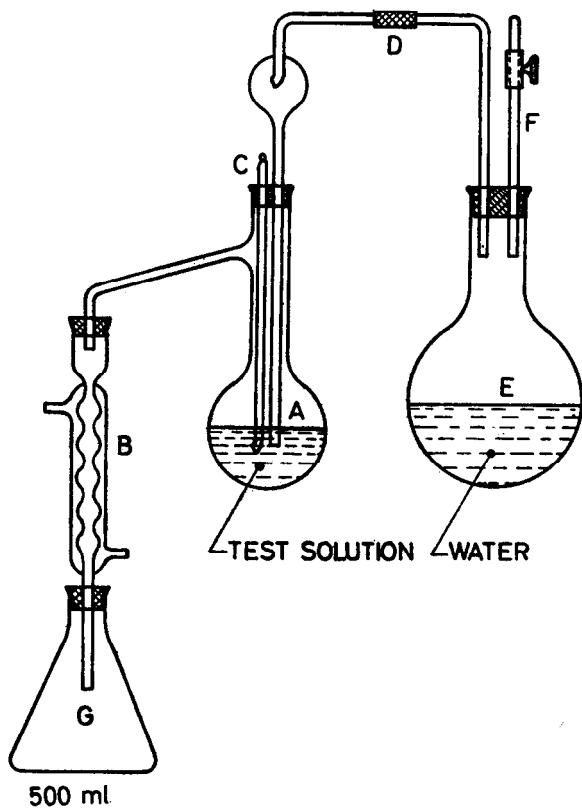


FIG. 1 APPARATUS FOR DISTILLATION OF FLUORINE

6.3 Reagents

6.3.1 *Perchloric Acid* — 70 percent.

6.3.2 *Sodium Alizarine Sulphonate Indicator* — Dissolve 0.050 g of alizarine sulphonate in 100 ml of water, and store in a dropping bottle.

6.3.3 *Sodium Hydroxide Solution* — Dissolve 20 g of sodium hydroxide pellets in water, cool and dilute to one litre. Mix well.

6.3.4 *Dilute Hydrochloric Acid* — Dilute 19.6 ml of concentrated hydrochloric acid ($rd = 1.16$) to 1000 ml with water. Mix well.

6.3.5 Buffer Solution — Dissolve 9.448 g of monochloroacetic acid in 100 ml of water. Add 50 ml of sodium hydroxide (1.0 N). Check the pH by pH meter. The pH should be 3.0 ± 0.1 .

6.3.6 Standard Thorium Nitrate Solution (0.025 M) — Dissolve 13.806 g of thorium nitrate $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$, in water and make up to one litre. Mix well. Standardize against standard sodium fluoride solution (see 6.3.7) and carry out all the stages of procedure given in 6.4.3. Preferably a calibration curve may be prepared showing volume of thorium nitrate titre against quantity of sodium fluoride.

6.3.7 Standard Sodium Fluoride Solution (1 ml = 1 mg of F) — Dissolve 2.211 g of sodium fluoride (AR), previously dried at 120°C to constant mass, in one litre of water in a volumetric flask.

6.4 Procedure

6.4.1 Transfer 0.5 g of an accurately weighed sample to a 250-ml distillation flask containing 0.5 g of sodium silicate and a few glass beads. Add 10 ml of perchloric acid. (Phosphoric acid may be used along with perchloric acid as it may help release of fluorine for the complex.)

6.4.2 Place a 1000-ml flask under the condenser. Connect the apparatus as shown in Fig. 1, distillation flask (A) to the condenser and distil the solution until the boiling point reaches 140°C . While this is being done heat the water in the steam generator (E) to boiling but do not allow the steam to get in the flask (A). When the temperature reaches 140°C , admit steam into the flask (A). Maintain the temperature at $140 \pm 2^\circ\text{C}$ by adjusting the steam flow and heating of the flask (A). Distil at such a rate that no fumes or mist escape from the volumetric flask. Continue distillation until nearly 250 ml are collected in a 100-ml flask.‡

6.4.3 Transfer to a 240-ml volumetric flask. Make the volume up to the mark and mix well. Pipette out 50-ml aliquot into a 250-ml beaker. Add 50 ml of water, 10 drops of sodium alizarine sulphonate indicator solution and mix. Add sodium hydroxide solution slowly with stirring till the solution becomes pink. Add dilute hydrochloric acid drop by drop with stirring till the pink colour is just discharged leaving the solution just acid. Add two millilitres of buffer solution and titrate with standard thorium nitrate solution with constant stirring, till a permanent pink end point is reached. The colour intensity at the end point should be kept in mind and the titration should be stopped exactly at the same colour intensity for both the standard thorium nitrate solution (see 6.3.6) and the test solution titration.

6.5 Calculation

$$\text{Fluorine, percent} = \frac{A \times B}{C} \times 100$$

where

A = volume in ml of standard thorium nitrate solution,

B = fluorine equivalent of the standard thorium nitrate solution in g/ml, and

C = mass in g of the sample represented by the aliquot taken.

7. DETERMINATION OF CARBON DIOXIDE

7.1 Outline of the Method — A known mass of the sample is made to react with an acid and the liberated carbon dioxide freed from impurities is absorbed in previously weighed soda asbestos bulbs and weighed. From the difference in masses the percentage of carbon dioxide is calculated.

7.2 Apparatus — The assembly of apparatus is shown in Fig. 2. In order to obtain better pressure for drawing gases through the train, all joints should be mercury sealed.

7.3 Reagents

7.3.1 Dilute Hydrochloric Acid — 1 : 1 (v/v).

7.3.2 Concentrated Sulphuric Acid — rd = 1.84 (conforming to IS : 266-1961*).

7.3.3 Ascarite or Soda Asbestos — solid.

7.3.4 Magnesium Perchlorate — solid.

7.3.5 Pumice Impregnated with Copper Sulphate — Anhydrous. Crush pumice to approximately 5 mm size, sift free from dust, and transfer 60 g to a casserole. Cover with a concentrated solution of 30 to 35 g of copper sulphate, evaporate to dryness while constantly stirring, and then heat for 3 to 4 hours at 150 to 160°C in an air-bath. Cool in a desiccator and preserve in a glass-stoppered bottle.

7.4 Procedure — Transfer 1 g of an accurately weighed sample to the flask A and cover it with water. Insert the stopper carrying the separatory funnel (B) and a condenser (C). Connect the latter with (D), (E) and (F). Pass air that is free from carbon dioxide through the system until it is judged that all carbon dioxide has been removed. Close the

*Specification for sulphuric acid (revised).

stop-cock in the separatory funnel, and insert the weighed absorption bulbs (*G*) and (*H*) in the train; *H'* acts as a guard tube. Half fill the separatory funnel with dilute hydrochloric acid, replace the stopper carrying the air, and see that there is free passage for gases through the train. Open the stop-cock in the separatory funnel and run acid into the flask slowly if there is much carbon dioxide, and rapidly if there is but little. When effervescence diminishes in the former case, at once in the latter, start a flow of water in the condenser and heat the flask slowly so as to secure steady but quiet ebullition. When it is judged that carbon dioxide has been boiled out of the solution, remove the flame, increase the current of air and sweep out all carbon dioxide. Disconnect the weighed bulbs, close the inlet and outlet tubes, and place them on the balance case. When cool, open the stopper momentarily and weigh.

7.5 Calculation

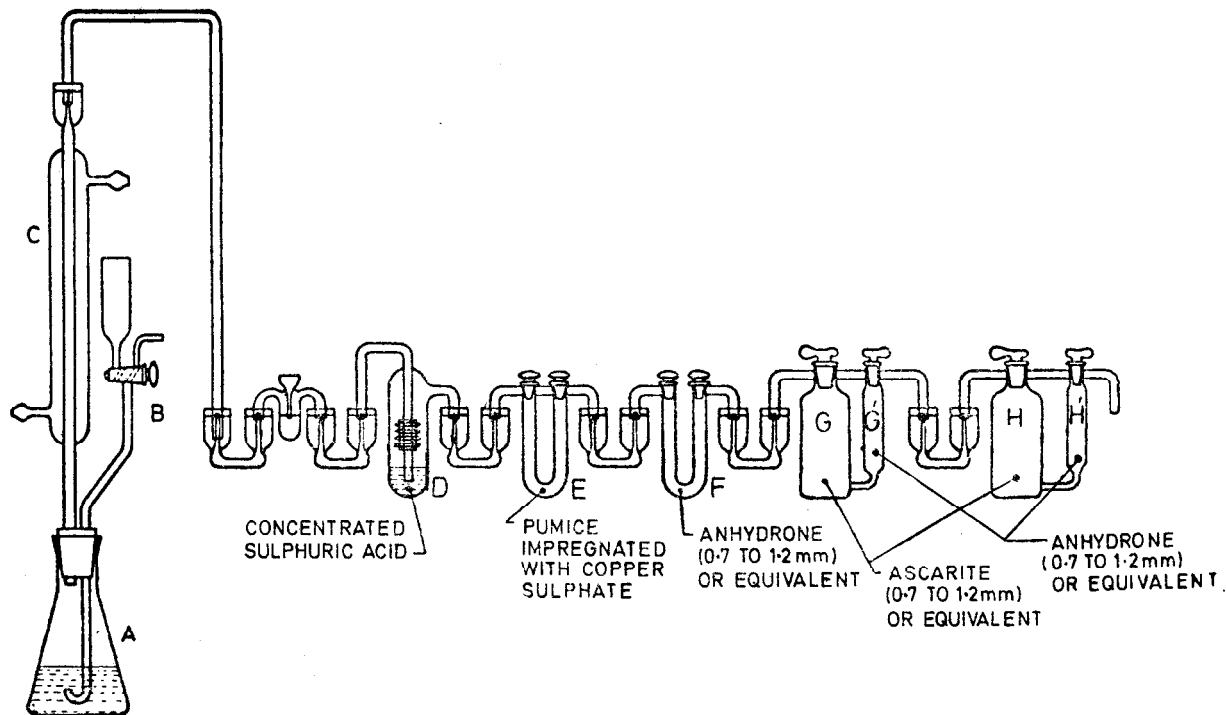
$$\text{Carbon dioxide, percent} = \frac{(A - B)}{C} \times 100$$

where

A = mass in g of the bulbs after the test,

B = mass in g of the bulbs before the test, and

C = mass in g of the sample taken.



NOTE — Tubes are compactly arranged along the edge of 150 × 230 mm board which is supported 130 mm from the table top upon a tripod base.

FIG. 2 ABSORPTION TRAIN FOR CARBON DIOXIDE